

**Diurnal variations of
reactive chlorine and
nitrogen oxides**

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Diurnal variations of reactive chlorine and nitrogen oxides observed by MIPAS-B inside the January 2010 Arctic vortex

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Abstract

The winter 2009/2010 was characterized by a strong Arctic vortex with extremely cold mid-winter temperatures in the lower stratosphere associated with an intense activation of reactive chlorine compounds (ClO_x). In order to assess the capacities of state-of-the-art chemistry models to predict polar stratospheric chemistry, stratospheric limb emission spectra were recorded during a flight of the balloon version of the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS-B) from Kiruna (Sweden) on 24 January 2010 inside the Arctic vortex. Several fast limb sequences of spectra (in time steps of about 10 min) were measured from nighttime photochemical equilibrium to local noon allowing the retrieval of chlorine- and nitrogen-containing species which change quickly their concentration around the terminator between night and day. Mixing ratios of species like ClO , NO_2 , and N_2O_5 show significant changes around sunrise, which are temporally delayed due to shadowing of the lower stratosphere by upper tropospheric and polar stratospheric clouds. ClO variations were derived for the first time from MIPAS-B spectra. Daytime ClO values of up to 1.6 ppbv are visible in a broad chlorine activated layer below 26 km correlated with low values (close to zero) of its reservoir species ClONO_2 . Observations are compared and discussed with calculations performed with the 3-dimensional Chemistry Climate Model EMAC (ECHAM5/MESSy Atmospheric Chemistry). Mixing ratios of the species ClO , NO_2 , and N_2O_5 are fairly well reproduced by the model during photochemical equilibrium. However, since the model assumes cloudless illumination, simulated concentration changes around sunrise start earlier but less quickly compared to the observed variation of the species concentration.

1 Introduction

Chemically active chlorine species ($\text{ClO}_x = \text{Cl} + \text{ClO} + 2 \text{ClOOCl}$), which are part of total inorganic chlorine Cl_y , play a dominant role in the catalytic destruction of

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stratospheric ozone at the end of the polar winter season when cold temperatures and polar stratospheric clouds (PSC) have previously enabled to produce chlorine compounds (mainly Cl₂) from its reservoir species (ClONO₂, HCl, and HOCl) via heterogeneous chemical reactions (Solomon et al., 1986). In the sunlit atmosphere, these compounds are being photolyzed to yield Cl atoms and subsequent chlorine monoxide (ClO). When high (daytime) ClO concentrations (≥0.5 ppbv) are present in the lower stratosphere the ClO-ClO dimer cycle governs (besides the ClO-BrO cycle) the destruction of polar ozone (see e.g. Molina et al., 1987; Brasseur and Solomon, 2005):



Taking into account Reaction (R4) twice in this scheme, the complete catalytic cycle leads to a net reduction of ozone by $2 \text{O}_3 + h\nu \rightarrow 3 \text{O}_2$. The diurnal variation of the concentration of ClO and its dimer is controlled by this reaction scheme. During night, high ClOOCI amounts of about 1 ppbv were observed in activated Arctic vortex air in situ (Stimpfle et al., 2004) and by remote sensing with the balloon-borne Michelson Interferometer for Passive Atmospheric sounding (MIPAS-B; Wetzel et al., 2010). During day, volume mixing ratios (VMR) below 0.5 ppbv have been measured inside the vortex by in-situ instruments in the lower stratosphere (Stimpfle et al., 2004; von Hobe et al., 2007). In contrast, high Arctic ClO daytime mixing ratios around 2 ppbv were inferred from satellite observations of the Microwave Limb Sounder (MLS; Santee et al., 2003, 2008) and MIPAS on ENVISAT (Glatthor et al., 2004) during time periods of chlorine activation. During nighttime, mixing ratios usually are not higher than 0.5 ppbv (Glatthor et al., 2004). By the end of the polar winter, increasing illumination enhances

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the production of NO₂ (mainly by HNO₃ photolysis and its reaction with OH) such that the competing reaction:



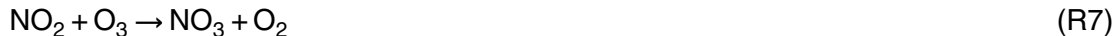
transfers active chlorine back into the important reservoir species ClONO₂ (see, e.g. Müller et al., 1994; Douglass et al., 1995). Hence, by the end of the Arctic winter, high values of more than 2 ppbv ClONO₂ have been measured (see e.g. Oelhaf et al., 1994; Dufour et al., 2006; Höpfner et al., 2007; Wetzel et al., 2010).

In the absence of sunlight in the deep polar winter, NO_x (NO + NO₂ + NO₃) is converted to the longer-lived reservoir species HNO₃, N₂O₅, and ClONO₂ in the gas phase. In cold winters, ClONO₂ and N₂O₅ are further converted to HNO₃ via heterogeneous reactions on particles of PSC. These reactions not only activate chlorine but also sequester HNO₃ into the particles which may settle down when they are large enough (Fahey et al., 2001). This redistribution leads to an irreversible removal of HNO₃ at higher altitudes (denitrification) together with an excess of HNO₃ due to evaporation at lower altitudes (renitrification). Intense denitrification events can thus delay ClONO₂ recovery via Reaction (R5) leading to an enhanced ozone destruction (see e.g. Waibel et al., 1999).

The species NO₂ in general regulates the ozone budget via reactions with radicals to form reservoir species like ClONO₂, HNO₃, N₂O₅, HO₂NO₂, and BrONO₂ which temporarily remove these radicals from ozone destroying reactions. NO₂ is in photochemical equilibrium with NO and N₂O₅. At sunset, NO is converted to NO₂ mainly via the reaction with ozone (see, e.g. Brasseur and Solomon, 2005):



followed by reactions producing N₂O₅:



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After sunrise, N_2O_5 is photolyzed back into NO_2 and NO_3 :



It can also be destroyed by collisional decomposition via the reverse of (R8). During day, NO_2 reacts rapidly to reform NO either by reaction with atomic oxygen (upper stratosphere) or photolysis:



Stratospheric NO_2 and N_2O_5 measurements have been carried out since many years. The first simultaneous MIPAS-B NO_2 and N_2O_5 measurement took place in February 1995 (Wetzel et al., 1997). Spatio-temporal variations of NO_2 , N_2O_5 , and other nitrogen-containing constituents were detected in the late winter Arctic vortex in March 2003 (Wiegele et al., 2009). Satellite observations of MIPAS on ENVISAT and the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) have shown the large variability of these species depending on diurnal illumination (see, e.g. Mengistu Tsidu et al., 2005; Funke et al., 2005; Wetzel et al., 2007; Kerzenmacher et al., 2008; Wolff et al., 2008). In this paper we focus on Arctic stratospheric mixing ratios of chlorine and nitrogen species which change quickly their concentration around the terminator between night and day. Retrieved trace gas profiles were deduced from limb emission spectra recorded around sunrise during a MIPAS-B flight from Kiruna (Sweden) on 24 January 2010 inside the activated polar vortex. These data are compared to the 3-dimensional Chemistry Climate Model (CCM) EMAC (ECHAM5/MESSy Atmospheric Chemistry model).

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2 MIPAS-B observations and meteorological situation

The balloon-borne limb-emission sounder MIPAS-B is a cryogenic Fourier Transform spectrometer which covers the mid-infrared spectral range from about 4 to 14 μm . MIPAS-B spectra are characterized by their high spectral resolution (about 0.07 cm^{-1} after apodization) which allows the separation of individual spectral lines from continuum-like emissions in combination with a high radiometric accuracy with a $1\text{-}\sigma$ gain error of typically 1%. Typical values of the noise equivalent spectral radiance (NESR) are within 1×10^{-9} and 7×10^{-9} $\text{W}/(\text{cm}^2 \text{sr cm}^{-1})$ for a single calibrated spectrum. Averaging over n ($n \leq 20$) spectra per single elevation scan reduces the spectral noise by a factor of $1/\sqrt{n}$. The instrument is distinguished by a high performance and flexibility of the pointing system with an after-all knowledge of the tangent altitude of better than 50 m at the $1\text{-}\sigma$ confidence limit. A comprehensive overview and description of the instrument together with processing of recorded interferograms to calibrated spectra including phase correction, Fast Fourier Transformation to the spectral domain, and two-point calibration of the spectra from arbitrary to radiance units is given by Friedl-Vallon et al. (2004) and references therein. It includes instrument characterization in terms of the instrumental line shape, field of view, NESR, line of sight of the instrument, detector nonlinearity and the error budget of the calibrated spectra.

The Arctic winter 2009/2010 started comparatively warm until the first half of December. However, from mid-December until end of January, temperatures in the lower stratosphere were unusually cold and fell below the frost point T_{ice} on a synoptic scale (Pitts et al., 2011). By the end of January, a major stratospheric warming initiated by a planetary wave number one developed which displaced the cold pool of air away from the centre of the vortex and marked the beginning of a gradual break-up of the vortex due to increasing baroclinity. However, temperatures at 30 hPa (~ 23 km) remained below the climatological mean until the end of January (Pitts et al., 2011). Even though the final warming of the vortex took already place in mid-February, the January 2010 winter was one of the coldest in the lower stratosphere during the last decades. The

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MIPAS-B flight took place on 24 January 2010 over northern Scandinavia inside the Arctic vortex at the beginning of this major warming. This phase of the vortex was dominated by liquid supercooled ternary solution (STS) PSC (Pitts et al., 2011). After the balloon was successfully launched from Esrang near Kiruna (Sweden) it reached its float level at about 34 km. All recorded limb sequences are depicted in Fig. 1. From nighttime photochemical equilibrium until local noon, several fast sequences of spectra were measured in time steps of about 10 min to allow the retrieval of photochemically active species which change quickly their concentration around the terminator between night and day (Seq. 05a–Seq. 09b; 06:16 UTC–10:20 UTC). For this purpose the line of sight of the instrument was aligned perpendicular to the azimuth direction of the sun to allow for a symmetric illumination of the sounded air mass before and beyond the tangent point. The variation of the solar zenith angle (SZA) during the observations is shown in Fig. 2. Local noon occurs at 09:57 UTC. All sequences exhibit some continuum-like emissions due to the occurrence of PSC in the spectra at altitudes below 25 km in line with low colour ratios of three different spectral regions as defined by Spang et al. (2004) and Höpfner et al. (2006). From these colour ratios, PSC seem to consist mainly of STS or small NAT (nitric acid trihydrate) particles with radii less than 3 μm or a mixture of both. 20 scans with different elevation angles from 34 km down to 13 km have been analyzed per sequence.

3 Data analysis and model calculations

Radiance calculations were performed with the Karlsruhe Optimized and Precise Radiative transfer Algorithm (KOPRA; Stiller et al., 2002) which is a line-by-line and layer-by-layer model to simulate the infra-red radiative transfer through the atmosphere. Molecular spectroscopic parameters for the calculation of limb emission spectra were taken from the HITRAN database (Rothman et al., 2005). KOPRA also calculates derivatives of the radiance spectrum with respect to atmospheric state and instrument parameters and thus provides the Jacobians for the retrieval procedure KOPRAFIT

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(Höpfner et al., 2002). While the vertical distance of observed tangent altitudes ranges between 0.8 and 1.5 km, the retrieval grid was set to 1 km up to the balloon float altitude. Above, the vertical spacing increases to 10 km at the upper altitude at 100 km. Taking into account the instrumental field of view, the retrieval grid is finer than the achievable vertical resolution of the measurement for a large part of the altitude region covered. To avoid retrieval instabilities due to this oversampling of the vertical retrieval grid, a Tikhonov-Phillips regularization approach (Phillips, 1962; Tikhonov, 1963) was applied which was constrained with respect to a height-constant zero a priori profile \mathbf{x}_a of the target species:

$$\mathbf{x}_{i+1} = \mathbf{x}_i + [\mathbf{K}_i^T \mathbf{S}_y^{-1} \mathbf{K}_i + \mathbf{R}]^{-1} [\mathbf{K}_i^T \mathbf{S}_y^{-1} (\mathbf{y}_{\text{meas}} - \mathbf{y}(\mathbf{x}_i)) - \mathbf{R}(\mathbf{x}_i - \mathbf{x}_a)] \quad (1)$$

where \mathbf{x}_{i+1} is the vector of the wanted state parameters \mathbf{x}_i for iteration $i + 1$; \mathbf{y}_{meas} is the measurement vector and $\mathbf{y}(\mathbf{x}_i)$ the calculation of the radiative transfer model using state parameters of iteration number i ; \mathbf{K} is the Jacobian matrix containing partial derivatives $\partial \mathbf{y}(\mathbf{x}_i) / \partial \mathbf{x}_i$ while \mathbf{S}_y^{-1} is the inverse noise measurement covariance matrix and \mathbf{R} a regularization matrix with the first derivative operator.

For the temperature retrieval, a first derivative a priori constraint was used. This state parameter was derived first by using appropriate CO_2 lines of two separate bands around 810 cm^{-1} and 950 cm^{-1} and a priori pressure-temperature information from ECMWF together with a CO_2 VMR profile updated with data from NOAA ESRL GMD (National Oceanic and Atmospheric Administration, Earth System Research Laboratory, Global Monitoring Division; Montzka et al., 1999). The temperature retrieval $1\text{-}\sigma$ accuracy is estimated to be within about 1 K. Then, VMR profiles of the target species are individually retrieved in selected spectral regions (see Table 1). A detailed overview on the analysis of nitrogen- and chlorine-containing molecules is given in Wetzel et al. (2002, 2010). The error estimation of the target parameter consists of random and systematic errors which were added quadratically to yield the total error which refers to the $1\text{-}\sigma$ confidence limit. Random errors include spectral noise as well as covariance effects of the simultaneously fitted parameters. Systematic errors mainly comprise

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spectroscopic data inaccuracies (band intensities), uncertainties in the line of sight, and gain calibration errors. The altitude resolution is calculated from the number of degrees of freedom of the retrieval which corresponds to the trace of the averaging kernel matrix. Typical values for the retrieved parameters are given in Table 1.

5 Measured MIPAS-B data are compared to simulations performed with the Chemistry Climate Model EMAC developed at the Max-Planck-Institute for Chemistry in Mainz (Jöckel et al., 2006). EMAC is a combination of the general circulation model ECHAM5 (Roeckner et al., 2006) and several submodels like the chemistry module MECCA (Sander et al., 2005) and the microphysical submodel PSC (Kirner et al., 2011) combined through the interface Modular Earth Submodel System (MESSy; Jöckel et al., 2005).

10 Data from a two years simulation until January 2010 with EMAC Version 1.10 were taken for this study. The simulation was carried out with a time step of 10 min and a T42 ($2.8^\circ \times 2.8^\circ$) horizontal resolution with 90 vertical layers from the surface up to 0.01 hPa (~ 80 km). A Newtonian relaxation technique of the prognostic variables temperature, vorticity, divergence and the surface pressure above the boundary layer and below 1 hPa towards ECMWF operational analysis has been applied in order to nudge the model dynamics towards the ECMWF one. Sensitivity studies with different EMAC runs have shown that nudging up to the upper stratosphere is important to reproduce the observed stratospheric temperature distribution which governs the formation of PSC and therefore the amount of active chlorine. The parameterization of NAT is based on the efficient growth and sedimentation of NAT particles as described in Kirner et al. (2011). The NAT formation takes place below the NAT condensation temperature (T_{NAT}) with the assumption of a necessary super cooling of 3 K. The STS formation is based on Carslaw et al. (1995) and takes place through uptake of nitric acid (HNO_3) by liquid sulphuric acid aerosols. Boundary conditions for greenhouse gases are from the IPCC-A1B scenario (IPCC, 2001) and adapted to observations from the AGAGE database (Prinn et al., 2001). Halogenated hydrocarbons are included according to the WMO-Ab scenario (WMO, 2007). The simulation includes a comprehensive chemistry

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5 setup from the troposphere to the lower mesosphere with 98 gas phase species, 178 gas phase reactions, 60 photolysis reactions, and 10 heterogeneous reactions on liquid aerosols, NAT- and ice particles. In comparison between the reactivity of NAT and liquid aerosols, the activation of ClO_x takes place mainly at liquid aerosols. The calculation of the photolysis rates is based on the fast on-line scheme by Landgraf and Crutzen (1998), which accounts for spherical geometry by employing an air mass factor correction with an extrapolation of the calculated photolysis rates for solar zenith angles between 88 and 94.5 degrees. Rate constants of gas-phase reactions are mainly taken from the compilation of Sander et al. (2003). For the photolysis rate calculation of ClOOCl the absorption cross sections recommended by Sander et al. (2006) have been taken. The model output data was saved every 10 min. The temporally closest output to the MIPAS-B measurements has been interpolated in space to the observed geolocations.

4 Results and discussion

15 In this section, profiles retrieved from MIPAS-B limb sequences measured before and after sunrise on 24 January 2010 are discussed and compared to chemical modelling. The sunrise took place between 06:44 UTC at 34 km and 07:19 UTC at 13 km altitude. Figure 3 shows the measured temperature cross section from 06:16 UTC to 10:20 UTC, corresponding to about $29^\circ \text{E}/69^\circ \text{N}$ and $34^\circ \text{E}/67^\circ \text{N}$. Very cold temperatures are visible in a broad layer between about 16 and 26 km which is slightly tilted from the western (left) to the eastern (right) part of the sounded vortex. This cold region was covered by numerous PSC mostly consisting of STS as seen by spaceborne lidar observations (Pitts et al., 2011). Two-days backward trajectories at 550 K (~ 23 km) show that the air parcels which were observed by MIPAS-B were transported inside the vortex and experienced cold temperatures below T_{NAT} most time of this period. Hence, a strong chemical activation of chlorine can be expected in the lower stratosphere.

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The temporal variation of the important chlorine species ClO is shown in Fig. 4. A broad layer with enhanced ClO mixing ratios is visible between 16 and 26 km which coincides with the layer of coldest temperatures (cf. Fig. 3). Mixing ratios of up to 1.6 ppbv are detected around 23 km. High daytime ClO values of up to 1.2 ppbv at 20 km have also been detected during a flight of the Geophysica aircraft over northern Scandinavia (Sumińska-Ebersoldt et al., 2012) on 30 January 2010. The diurnal variation of the concentration of ClO in the lower stratosphere is controlled by reaction scheme (R1) to (R4). Related to the sunrise terminator, the strong increase of the ClO concentration due to photolysis of ClOOCl (R2) is delayed in the observations by about 45 min. The terminator refers to the sunrise under cloudless conditions. However, upper tropospheric clouds were present in South-East direction towards the rising sun, which were detected by Meteosat (06:00 UTC) and the Moderate Resolution Imaging Spectroradiometer (MODIS) aboard the Terra satellite (overpass at 09:17 UTC). Calculations for local sunrise (including refraction) show that a cloud top height of about 8 km delays the sunrise by approximately 20 min at this latitude and season. The residual time difference might be explained by shadowing of numerous PSC which were present in the altitude region of the ClO maximum. A more quantitative study of the delay in the onset of ClOOCl photolysis is subject of an additional study. Figure 5 shows the simulated variation of ClO as calculated by the chemical model EMAC. The simulated ClO layer peaks at the same altitude as the measured one does and calculated mixing ratios at 23 km are roughly the same as in the observation. Since cloudless conditions are assumed for the calculation of photochemical processes, the increase of ClO starts already around sunrise, but with slower velocity compared to the MIPAS-B measurement. In the case of the observation, the SZA marking the starting illumination is already smaller when the sun rises above the clouds compared to the cloudless case. This results in a faster increase of the ClO concentration. However, observed and modelled ClO daytime equilibrium values are reached at the same time with equal value. Besides the altitude of the ClO maximum, also the vertical extension of the enhanced ClO is very well reproduced by the model.

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The modelled variation of the chlorine monoxide dimer ClOOCl is depicted in Fig. 6. The diurnal variation of the amount of ClOOCl and ClO is governed by reaction scheme (R1) to (R4). High nighttime values close to 1.0 ppbv are calculated by the model. The photodissociation of ClOOCl in favour of the production of ClO starts at sunrise in the model. Unfortunately, the dimer ClOOCl could not be unambiguously inferred from MIPAS-B spectra of this flight since the continuum-like emission of the ClOOCl ν_1 band cannot be separated from the quasi-continuum emission induced by PSC particles in the corresponding altitude region. MIPAS-B observations under comparable conditions in an activated chlorine layer (without PSC) in January 2001 revealed nighttime ClOOCl mixing ratios of nearly 1.1 ppbv at 20 km (Wetzel et al., 2010) which are of comparable magnitude. The resulting ClO_x in the model is about 2.1 ppbv at its maximum. Taking also into account the species HOCl and OCIO, total ClO_x values increase to 2.2 ppbv at 23 km. While OCIO is not measurable by MIPAS-B, mean HOCl values (averaged over all measured sequences) amount to 0.2 ppbv in this altitude region.

Large amounts of ClO_x are typically connected with low amounts of the chlorine reservoir gas ClONO₂ since the maximum of inorganic chlorine (Cl_y = ClO_x + ClONO₂ + HCl + minor components) is a conserved quantity within the timeframe of one winter. Measured ClONO₂ amounts are depicted in Fig. 7. ClONO₂ values of up to 1.5 ppbv, which are not unusual for mid-winter conditions (Dufour et al., 2006), were measured at 27 km. However, downwards from 25 km ClONO₂ mixing ratios fall to values close to zero, coincident with the region of high ClO_x amounts. The ClONO₂ simulation by EMAC (see Fig. 8) yields significantly smaller mixing ratios of only 1.1 ppbv as compared to the MIPAS-B observation, but at least in the same altitude region. At 26 km, simulated HCl mixing ratios are close to 1.8 ppbv. Hence, the partitioning between the chlorine reservoir species ClONO₂ and HCl (which cannot be measured by MIPAS-B) seems to be shifted towards more HCl in the model compared to the observation (provided that the modelled Cl_y is correct). Considering the zonal mean of the ratio between HCl and ClONO₂ near 68° N, we find that, around 26 km, this quantity has not been changed significantly in the model between autumn 2009 and the time of the

MIPAS-B observation. Simulated Cl_y amounts to 3.2 ppbv at 26 km. Total Cl_y can be estimated from measured N_2O with the help of a N_2O - Cl_y relationship as described by Wetzel et al. (2010). Taking into account a -0.9% per year Cl_y decrease since 2001 (WMO, 2011) we can confirm the EMAC value by estimating about 3.2 ppbv Cl_y from the MIPAS-B N_2O observations at 26 km. Both, measurement and calculation exhibit a temporal decrease of the ClONO_2 concentration from nighttime to local noon. This can be, at least to a large extent, attributed to the diurnal cycle of this species due to photolysis of ClONO_2 after sunrise to produce NO_3 and atomic Cl which will react mainly with O_3 to form ClO, and thus ClO_x slightly increases after sunrise.

The molecule ClONO_2 is also linked to the nitrogen family. As mentioned earlier, the availability of the species NO_2 is important for the build-up of ClONO_2 via Reaction (R5). NO_2 is known to have a strong diurnal variation dependent on the SZA. The measured NO_2 variation around sunrise is shown in Fig. 9. A strong decrease of NO_2 about 30 min after sunrise is visible at altitudes above 30 km. As mentioned before, upper tropospheric clouds with a top height of about 8 km delay the sunrise by 20 min. Since the NO_2 maximum is located above and not (like in the case of ClO) in the PSC layer, the cloud attenuation of solar illumination during and after sunrise is weaker as in the ClO case. During daylight, NO_2 is quickly transformed into NO via Reactions (R11) and (R12). The corresponding model calculation is depicted in Fig. 10. As expected, the simulated photodissociation of NO_2 starts near sunrise because the model assumes cloudless conditions for the illumination. Modelled day- and nighttime quantities of NO_2 are comparable to the measured ones but simulated temporal and vertical gradients are smaller than in the observation. This might be explained by numerical smoothing (time steps and vertical resolution) in the simulation and the steady rising (cloudless) illumination in the model simulation. The measurement clearly exhibits the slow daytime increase of NO_2 arising from the photolysis of N_2O_5 according to Reactions (R9) and (R10). This increase appears to be slightly weaker in the model calculation.

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The observed temporal evolution of N_2O_5 is illustrated in Fig. 11. Nighttime values close to 0.9 ppbv were measured just before sunrise where N_2O_5 reaches its diurnal maximum. The photolysis of N_2O_5 corresponding to (R9) begins shortly after sunrise. In accordance with theory, the photolysis rate is much slower than in the case of NO_2 . Hence, the delayed sunrise due to clouds is hardly visible in the photodissociation frequency of N_2O_5 . The corresponding EMAC simulation is displayed in Fig. 12. The agreement with measured N_2O_5 is close to perfect above 26 km. This holds not only for the magnitude and altitude of the VMR maximum but also for the frequency of photodissociation. Below 26 km, however, the model seems to convert too much N_2O_5 into HNO_3 by heterogeneous hydrolysis of N_2O_5 which takes place on sulphate aerosols and particles of PSC. Further studies are required to investigate these differences.

5 Conclusions

The winter 2009/2010 was characterized by a strong polar vortex with extremely cold temperatures in the lower Arctic stratosphere in mid-winter. MIPAS-B limb emission measurements were carried out on 24 January 2010 just before a stratospheric warming induced rising temperatures. Low temperatures and concomitant PSC formation produced considerable amounts of active chlorine (ClO_x) in a broad layer of the lower stratosphere between about 16 and 26 km which correlate with low quantities of its reservoir species ClONO_2 . The strong temporal change in ClO mixing ratios around the terminator between night and day was observed by MIPAS-B for the first time. This concentration change is also visible in the simulation of the CCM EMAC. The time delay in the ClO build-up between MIPAS-B and EMAC could be reduced if the model would be able to simulate reduced illumination caused by shadowing of clouds. Anyhow, measured and modelled daytime equilibrium ClO mixing ratios (about 1.6 ppbv) are in perfect agreement. To calculate correct chlorine activation in the sounded air masses, the temperature history of the air parcels is an important issue, because it is crucial whether PSC have been formed resulting in chlorine activation at their particle surfaces.

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The photochemically active nitrogen containing molecules NO_2 and N_2O_5 are correlated with each other and exhibit the expected changes after sunrise. While the comparatively slow N_2O_5 variation above 26 km is nearly perfectly reproduced by EMAC, the quick change in NO_2 mixing ratios proceeds slower compared to the observation.

The faster photodissociation rate in the measurement can be explained by the delayed but enhanced illumination when the sun is rising above upper tropospheric and stratospheric clouds (due to the lower sunrise SZA compared to cloudless conditions).

We conclude that during times of photochemical equilibrium the modelling of chlorine and nitrogen containing species is well performed by EMAC. Time differences in beginning alterations of mixing ratios due to starting illumination near the terminator between night and day are tentatively explained by shadowing of clouds which are not considered in the model simulations. A quantitative study of the delayed onset of photolysis will be subject of a separate study. Heterogeneous chlorine activation, which is strongly dependent on the correct modelling of stratospheric temperatures and PSC, is also captured by EMAC quite well. However, these overall encouraging results have to be verified for other winters.

Acknowledgements. We are grateful to the Swedish Space Corporation (SSC) launching team at Esrange for excellent balloon operations and logistical assistance and the Free University of Berlin for meteorological support (especially K. Grunow). This work was funded in part by the European Space Agency (ESA) and the German Aerospace Center (DLR).

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Table 1. Set-up for MIPAS-B trace gas retrievals and typical errors. Results are given for different state parameters in corresponding spectral windows together with the retrieval altitude resolution (Alt. reso.).

Species	Spectral range (cm ⁻¹)	Noise error ^a (%)	Total error ^a (%)	Alt. reso. (km)
ClO	821.0–841.5	10–50 ^b	15–50 ^b	3–5
ClONO ₂	779.7–780.7	2	6	2–3
NO ₂	1585.0–1615.0	3–6	10–12	2–4
N ₂ O ₅	1220.0–1270.0	2	6	3–5

^a In the altitude region of the VMR maximum;

^b daytime errors smaller than nighttime errors.

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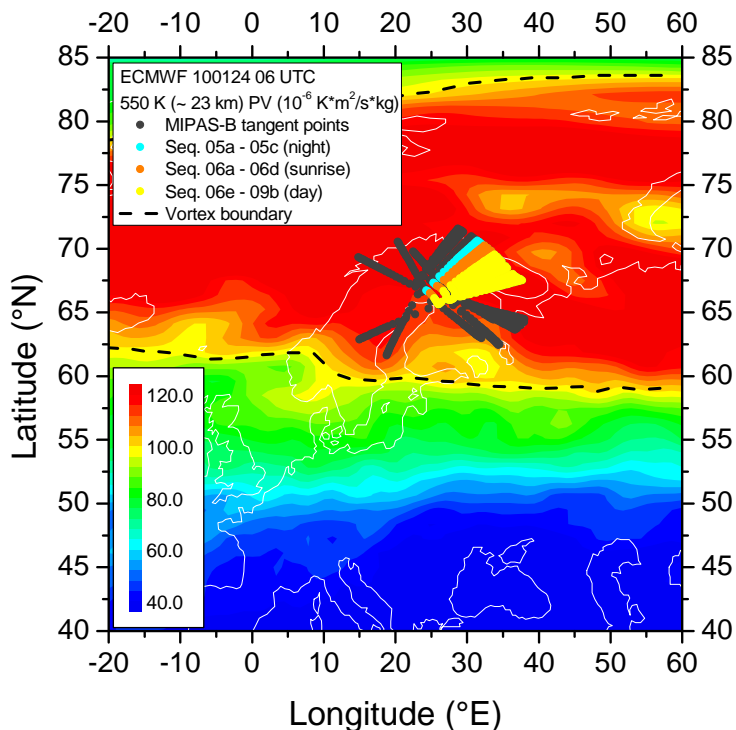


Fig. 1. Potential vorticity (PV) field from European Centre for Medium-Range Weather Forecasts (ECMWF) analysis on 24 January 2010, 06:00 UTC. MIPAS-B tangent points are plotted as solid circles. Sequences observed during night, close to sunrise, and during day are marked with different colours. The vortex boundary which represents the strongest PV gradient (Nash et al., 1996) is shown as dashed line.

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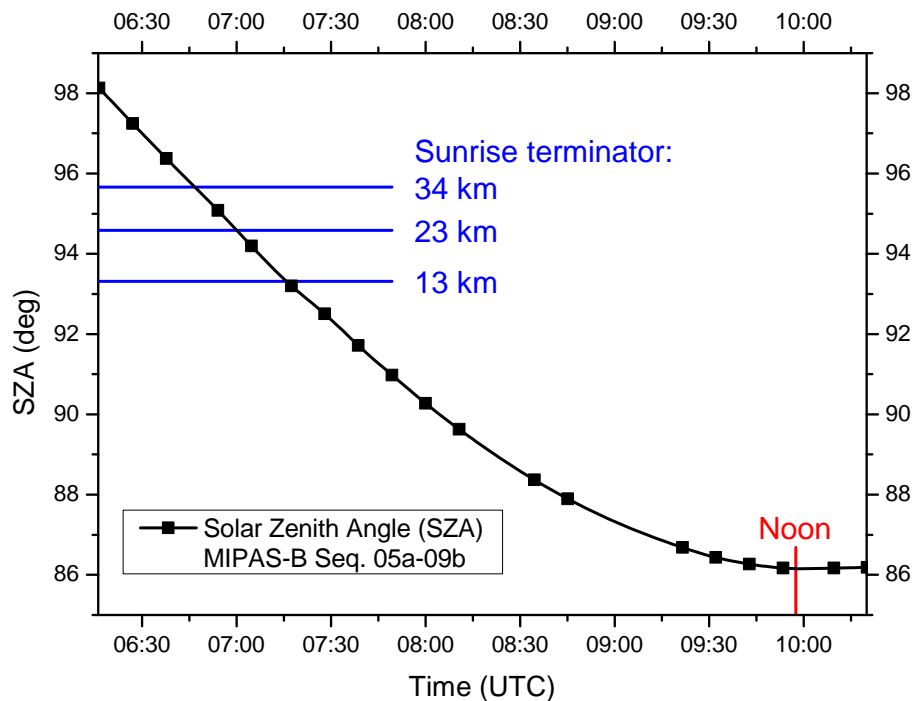


Fig. 2. Variation of the solar zenith angle (SZA) for MIPAS-B measured limb sequences 05a–09b (24 January 2010). Each black square denotes one recorded limb sequence. Altitude dependent local sunrise is given by the intersection of the black SZA line with the corresponding blue horizontal lines. Local noon is marked by a red line.

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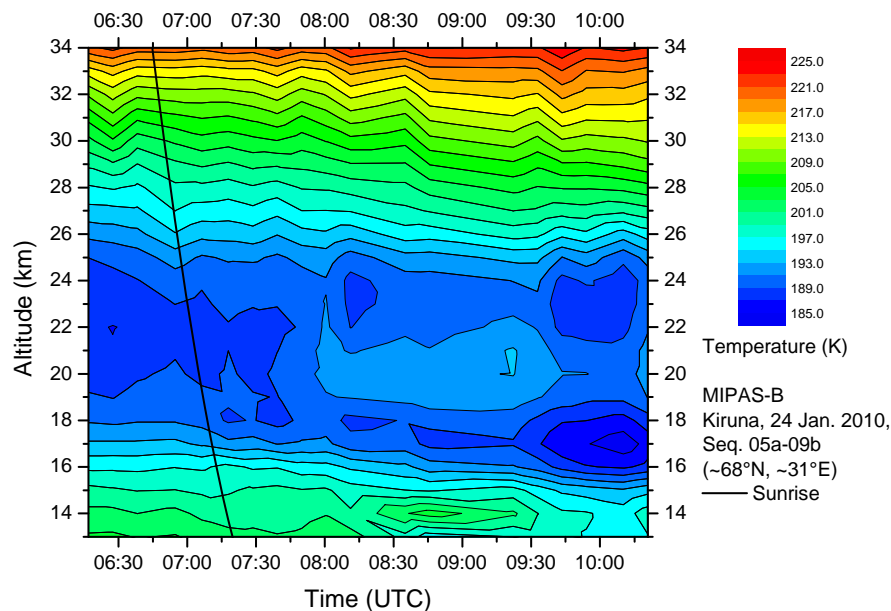


Fig. 3. Temperature as observed by MIPAS-B on 24 January 2010 above northern Scandinavia between 06:16 UTC and 10:20 UTC inside the Arctic vortex within the longitude/latitude sector shown in Fig. 1. The black solid line marks the sunrise terminator. Temperatures of less than 191 K occurred over a wide altitude region between about 16 and 26 km.

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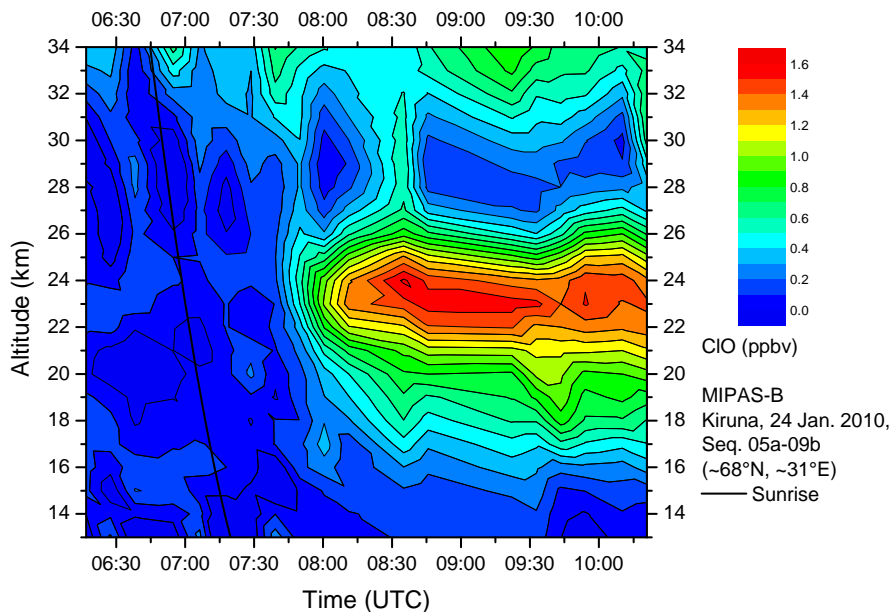


Fig. 4. Temporal evolution of chlorine monoxide (ClO) as observed by MIPAS-B on 24 January 2010 above northern Scandinavia. A broad ClO layer with a pronounced ClO maximum of more than 1.6 ppbv is visible. The strong photochemically induced increase in ClO mixing ratios starts about 45 min after sunrise presumably due to the occurrence of tropospheric and stratospheric clouds. For details, see text.

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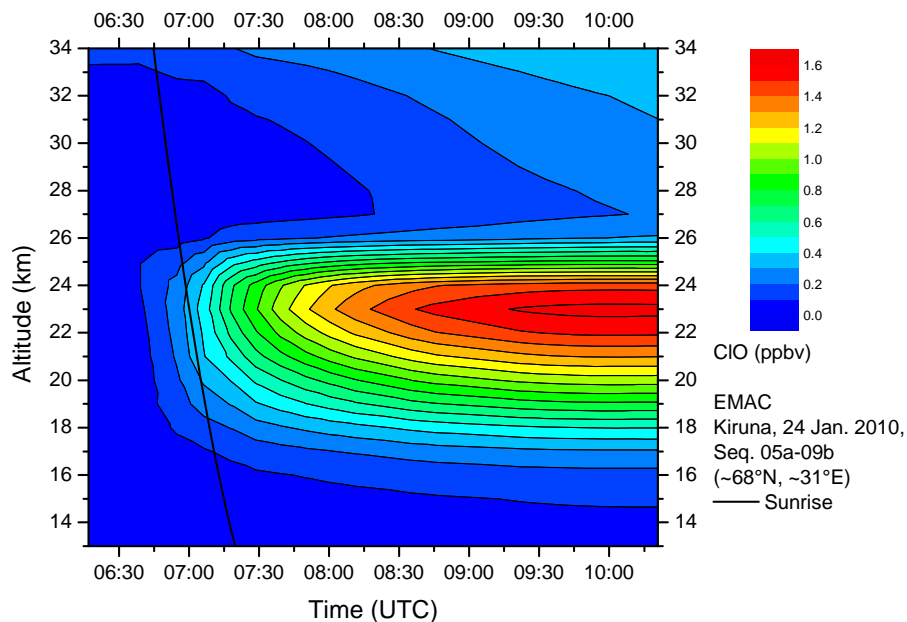


Fig. 5. Temporal evolution of CIO on 24 January 2010 as simulated by the chemical model EMAC. The build-up of CIO starts around sunrise. Maximum values of more than 1.6 ppbv are reached during daytime.

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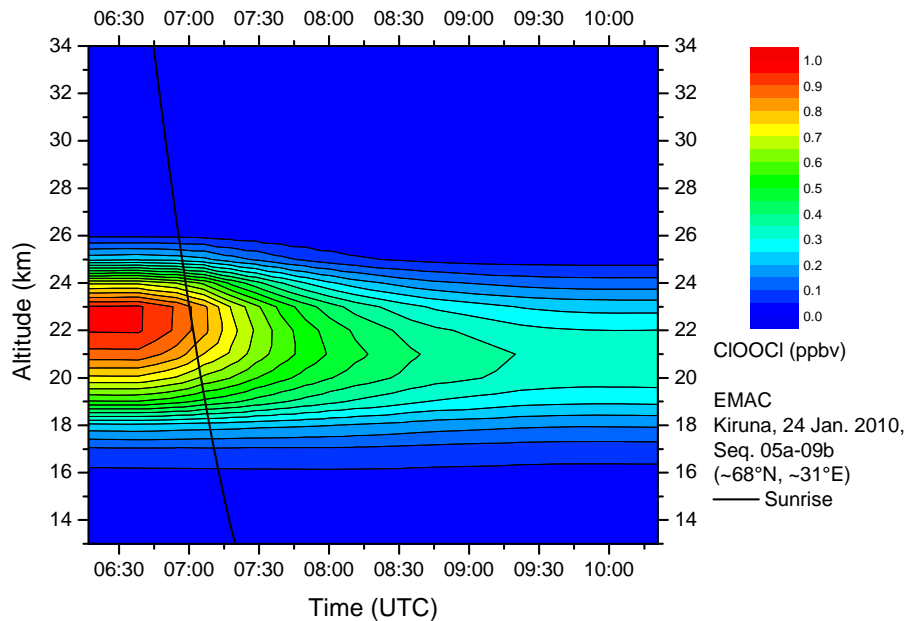


Fig. 6. Simulation of the chlorine monoxide dimer ClOOCl at the MIPAS-B measurement locations. The photodissociation starts at sunrise. For details, see text.

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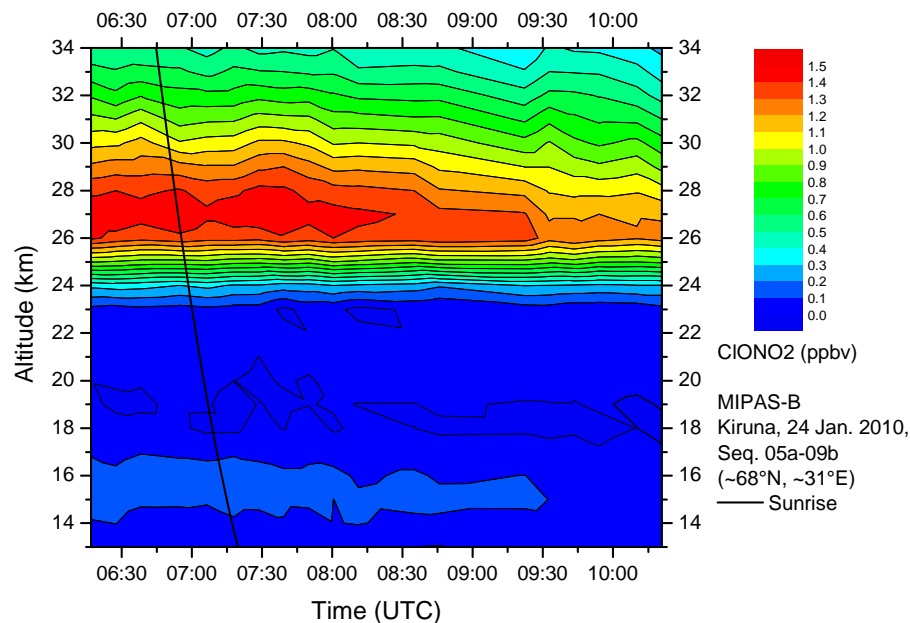


Fig. 7. CIONO₂ mixing ratios as seen by MIPAS-B above northern Scandinavia on 24 January 2010 inside the polar vortex. Very low CIONO₂ values below 24 km coincide with high amounts of activated chlorine.

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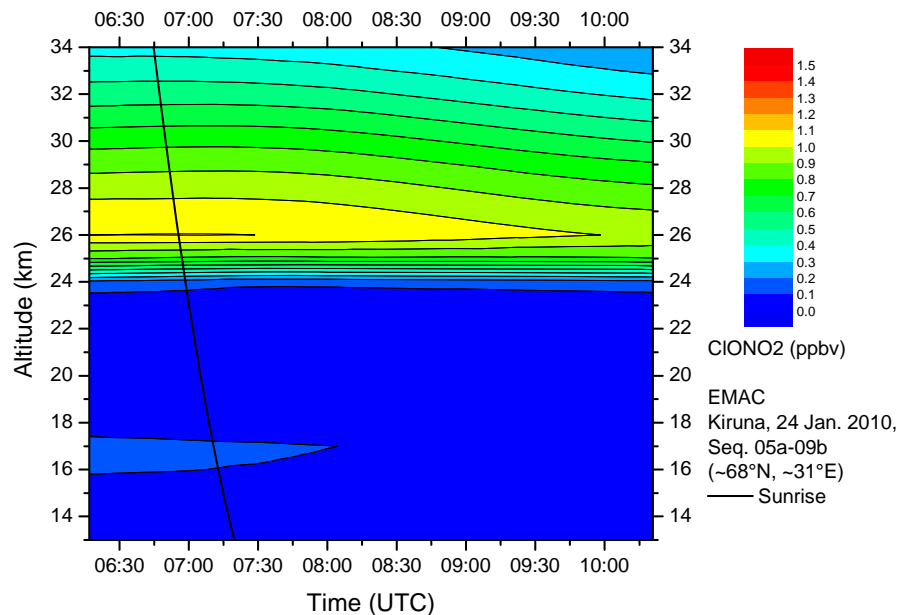


Fig. 8. CIONO₂ mixing ratios on 24 January 2010 as simulated by the CCM EMAC.

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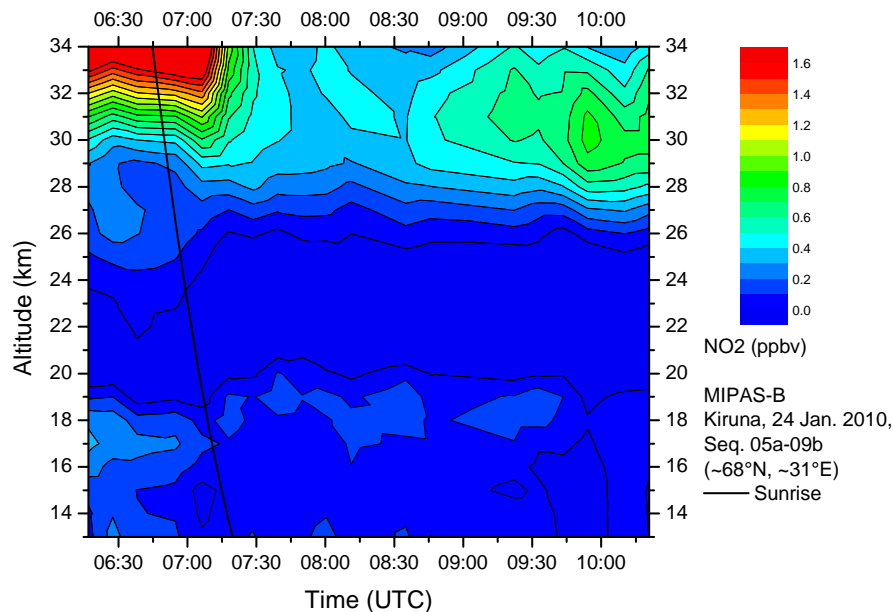


Fig. 9. NO₂ mixing ratios retrieved from MIPAS-B spectra recorded around sunrise on 24 January 2010. The strong photochemically induced decrease of NO₂ mixing ratios starts about 30 min after sunrise followed by a slower increase of NO₂ amounts due to N₂O₅ photolysis. For details, see text.

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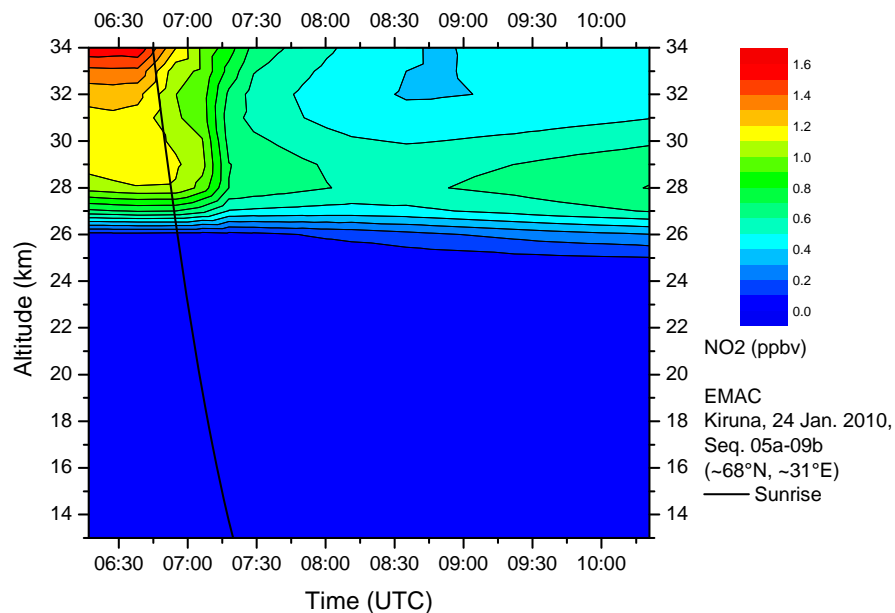
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**Fig. 10.** Temporal evolution of NO₂ amounts as calculated by EMAC.

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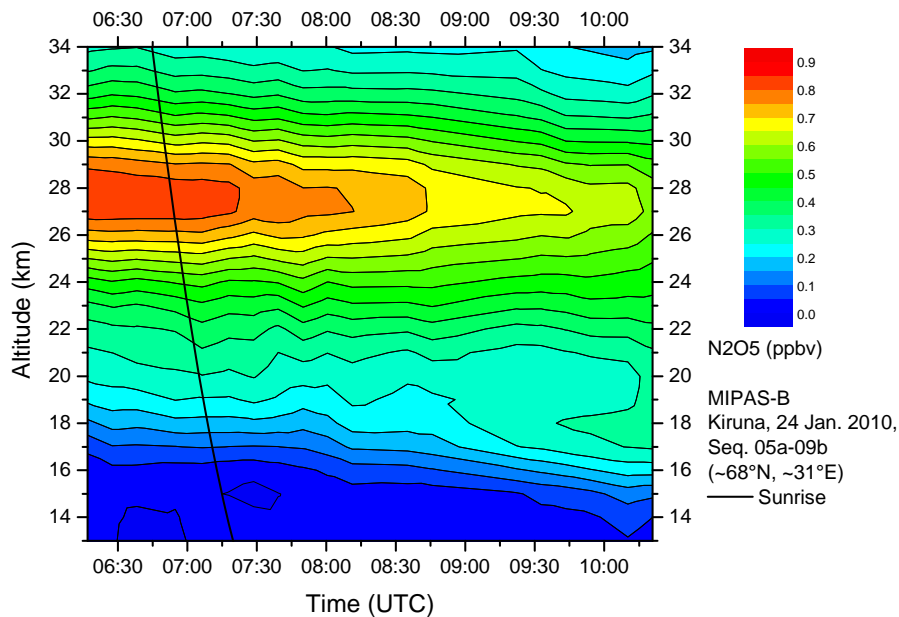


Fig. 11. N_2O_5 mixing ratios as measured by MIPAS-B on 24 January 2010 above northern Scandinavia. For details, see text.

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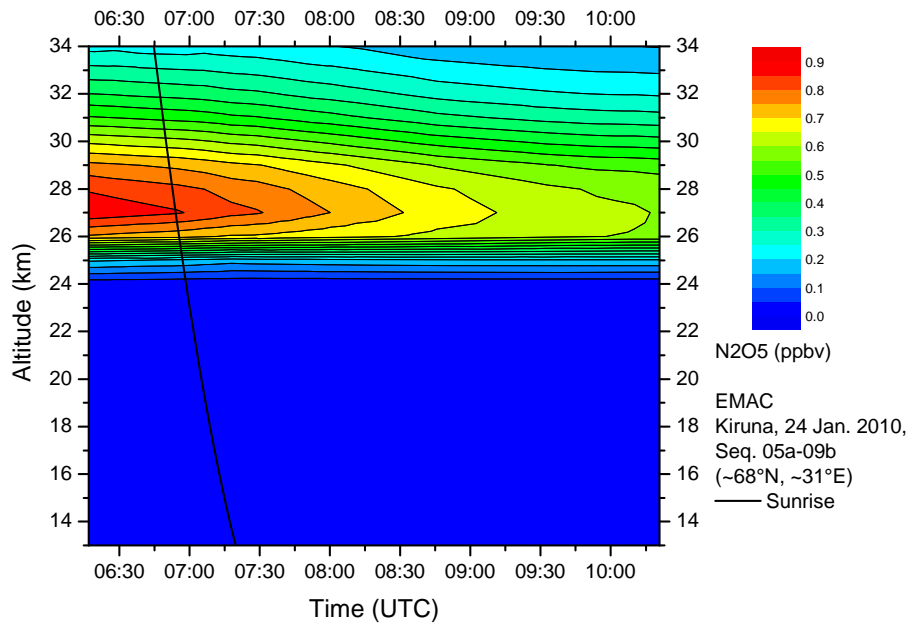


Fig. 12. Temporal evolution of N_2O_5 mixing ratios as calculated by EMAC.

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